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Contract Nonr. 736(000) Project Nr. 330-027

TECHNICAL REPORT No. 5

- I. Light Scattering of spherical colloidal particles.

Wilfried Heller and William J. Pangonis

- II. The determination of particle size and refractive index near the turbidity maximum in monodisperse suspensions of spherical particles.

Wilfried Heller

Submitted by W. Heller, Project Director
Chemistry Department, Wayne University
Detroit, Michigan

June 30, 1954

OFFICE OF NAVAL RESEARCH
Contract No. 736(00) Project NR 330-027

Research on the Size and Shape of Large
Molecules and Colloidal Particles

Technical Report No. 5

I. LIGHT SCATTERING OF SPHERICAL COLLOIDAL PARTICLES

By Wilfried Heller and William J. Pangonis

II. THE DETERMINATION OF PARTICLE SIZE AND REFRACTIVE INDEX NEAR THE TURBIDITY
MAXIMUM IN MONODISPERSE SUSPENSIONS OF SPHERICAL PARTICLES

By Wilfried Heller

Chemistry Department
Wayne University
Detroit, Michigan

June 30, 1954

Introductory Remarks

Part I of this Technical Report is a reprint, in mimeographed form, of a LETTER TO THE EDITOR which appeared in the May issue of the Journal of Chemical Physics (page 948). It is essentially a condensation of material brought in Technical Report I except for the inclusion of numerical turbidity data pertinent to $\alpha = 6.0$ (0.2) 7.0.

Part II contains turbidity data covering the additional range of $\alpha = 8.0$ (1.0) 15, calculated on the basis of the primary scattering functions given in Technical Report 3, and a series of remarks and statements regarding turbidity data obtained on correspondingly large particles (lower microscopic range). Part II is being submitted for publication to the same periodical.

Wilfried Heller

I. LIGHT SCATTERING OF SPHERICAL COLLOIDAL PARTICLES*

By Wilfried Heller and William J. Pangonis**

Chemistry Department, Wayne University, Detroit, Michigan

The Mie equations were used for obtaining the following quantities for spherical colloidal particles, considering $\alpha = 0.2$ (0.2) 7.0 and $m = 1.05$ (0.05) 1.30¹: (a) the reduced specific turbidity, $(\tau/c)_o$; (b) the reduced specific scattering at an angle of 90°, $(I_{90}/I_{0\pi})_o$; (c) the "scattering ratio", at 90°, for orthogonal electric vectors of the incident beam, $(I_{\perp\perp}/I_{\perp\parallel})_o$; (d,e) the mean "wave length exponents" of (a) and (b)², $(\Delta \log f(\lambda)/\Delta \log \lambda)_o$, for the λ_o -range 4370-5461 A.U.; (f,g) the differential exponents of (a) and (b), $(d \log f(\lambda)/d \log \lambda)_o$, at 5461 A.U.; (h) the intensity ratio at two selected symmetrical angles, $(I_{45}/I_{135})_o$ (dissymmetry). These data have been reported at several occasions³, but a detailed publication had to be delayed repeatedly for purely external reasons. For practical size determinations on colloidal particles, dispersed in a liquid, the specific turbidities are of primary interest because they alone were found to follow a monotonic curve throughout the major part of the colloidal range. In addition, the experimental method involved is quite simple⁴. Pending publication of the entire material, the latter data are made available, for general application, in the following Table I. They apply to the green mercury line (5461 A.U.), assuming a density of 1.000 for the scattering material. Division of these data by the actual density makes them applicable to any system within the range of α - and m - values defined⁵, provided the medium is water at 25°C.

* This work was carried out with the support of the Office of Naval Research.

** Present address: Film Department, E. I. DuPont de Nemours and Company, Buffalo, New York.

Table 1
 $(\text{C}/\text{c}) \cdot \text{cm}^{-1}$

α	m	1.05	1.10	1.15	1.20	1.25	1.30
0.2	0.0263	0.1040	0.2288	0.3978	0.6076	0.8540	
0.4	0.2025	0.8005	1.7761	3.1069	4.7698	6.7694	
0.6	0.6376	2.5411	5.6852	10.027	15.523	22.109	
0.8	1.3671	5.5159	12.454	22.184	34.617	49.723	
1.0	2.3645	9.5908	21.828	39.619	61.643	89.097	
1.2	3.5203	14.353	32.814	59.068	93.263	135.28	
1.4	4.7236	19.282	44.099	79.348	125.17	181.35	
1.6	5.9352	24.010	54.640	98.447	155.16	224.99	
1.8	7.0003	28.509	65.114	117.29	186.01	272.59	
2.0	8.0964	33.091	76.074	138.45	222.61	331.40	
2.2	9.2485	38.118	88.593	163.14	264.70	394.62	
2.4	10.535	43.701	102.37	188.99	304.45	445.31	
2.6	11.853	49.597	116.07	212.21	335.79	480.93	
2.8	13.242	55.175	128.44	231.64	361.83	516.16	
3.0	14.606	60.684	139.54	249.77	389.76	566.50	
3.2	15.912	65.704	150.37	268.79	420.70	599.77	
3.4	17.163	70.647	161.62	289.31	449.05	628.54	
3.6	18.395	75.731	173.10	308.04	471.44	649.12	
3.8	19.640	80.843	184.19	324.57	491.12	672.86	
4.0	20.909	85.960	194.79	340.06	511.84	698.60	
4.2	22.192	90.953	204.63	355.49	535.93	714.94	
4.4	23.473	95.805	214.40	370.17	547.15	721.95	
4.6	24.819	100.52	223.82	383.14	559.21	731.21	
4.8	25.970	105.16	232.56	385.04	572.03	744.09	
5.0	27.192	109.70	241.46	407.42	585.25	747.86	
5.2	28.389	114.28	250.02	418.73	593.98	740.82	
5.4	29.592	118.71	258.59	429.47	597.38	735.74	
5.6	31.040	123.19	266.45	436.07	600.58	737.13	
5.8	32.038	127.55	273.96	442.96	606.82	735.14	
6.0	33.239	131.74	280.23	450.88	611.78	720.27	
6.2	34.397	135.58	286.68	457.17	609.19	698.69	
6.4	35.564	139.54	293.40	463.43	603.39	687.61	
6.6	36.699	143.53	299.82	466.29	600.75	681.43	
6.8	37.855	147.49	305.15	469.06	599.60	661.32	
7.0	39.126	152.46	310.44	472.51	593.77	630.50	

Comparison of these data with extensive experimental results obtained in this laboratory on 20 monodisperse Dow polystyrene and polyvinyl toluene latices--first by J. N. Epel⁶ and later on by R. Tabibian⁷-- showed excellent agreement with electron microscopic data for particle diameters up to 2500 Å. U. and an agreement within about 10 per cent for much larger particles (up to 7700 Å. U.), using a precision apparatus constructed in this laboratory in conjunction with K. Herrington⁸.

References

1. $\alpha = d \frac{m}{\lambda}$, where d is the diameter of the particles and λ is the actual wave length in the scattering system; m is the refractive index of the scattering material relative to that of the medium.
2. W. Heller and E. Vassy; J. Chem. Physics; 14, 565 (1946).
3. E.g., Intern. Congress of Pure and Applied Chemistry; Sept. 10-13, 1951; New York, N. Y.; Phys. Rev.; 86, 645 (1952); Congress on "Radiations et Macromolecules", University of Strasbourg, France, June 9-11, 1952.
4. W. Heller and H. B. Klevens; Phys. Rev.; 67, 61 (1945).
5. $\alpha = 7.0$ corresponds to a diameter of 9131 A.U. for $\lambda_0 = 5461$ A.U. if the dispersing medium is water at 25° C. Extension of the data, up to a diameter of 13,000 A.U. is now in progress in collaboration with the Wayne University Computation Laboratory.
6. W. Heller and J. N. Eobel; Intern. Congress of Pure and Applied Chemistry; Sept. 1951; New York, N. Y.
7. W. Heller and R. Tabibian; 125th Meeting of the American Chemical Society; March 1954; Kansas City, Kansas.
8. W. Heller and K. Herrington; 116th Meeting of the American Chemical Society; Sept. 1949; Atlantic City, N. J.

II. THE DETERMINATION OF PARTICLE SIZE AND REFRACTIVE INDEX NEAR THE TURBIDITY
MAXIMUM IN MONODISPERSE SUSPENSIONS OF SPHERICAL PARTICLES.*

Wilfried Heller

Chemistry Department, Wayne University, Detroit, Michigan

A preceding preliminary publication (1) gave the specific turbidity, $(\bar{\tau}/c)_0$, for colloidal solutions of non-absorbing spherical particles as derived from the Mie-theory. These data have now been extended to include also the lower range of microscopic diameters (up to 1.96 microns if the wavelength, in vacuo, $\lambda_0 = 5461 \text{ A.U.}$) and are given in Table I (2)(3).

Table I

$(\bar{\tau}/c)_0 \text{ cm}^{-1}$

α^m	1.15	1.20	1.25
8	331.500	473.482	544.076
9	343.447	456.120	471.681
10	346.898	423.747	390.457
11	342.648	380.572	312.353
12	331.531	331.282	245.654
13	314.536	280.618	193.651
14	292.941	232.722	156.163
15	262.770	190.811	132.999

The monotonic character of the curves observed throughout the major part of the colloidal range (1) ceases here, except for $m = 1.05$, due to the appearance of the first turbidity maximum. Consequently, experimental $(\bar{\tau}/c)_0$ - data become bivalued with regard to coordinated particle diameters, D , in microns, as illustrated in Table 2 for $m = 1.20$ and $\lambda_0 = 5461 \text{ A.U.}$

Table 2

$(\bar{\tau}/c)_c$:	350	370	390	410	430	450	470
D_1 :	1.5198	1.465	1.409	1.348	1.288	1.208	1.080
D_2 :	.5375	.5675	.6092	.6575	.7136	.7775	.8845

A suitable criterion is then necessary in order to decide whether a given $(\bar{\tau}/c)_c$ is associated with the ascending or descending branch of the turbidity curve. The simplest solution is a second turbidity measurement carried out at a different wave length, say at 4358 A.U. If the alternate $(\bar{\tau}/c)_c$ - value is smaller, then the larger particle size applies. It is, of course, possible to expand this to the compilation of a "turbidity spectrum" (4) which furnishes the "wave length exponent" (5) as an entirely independent measure of particle size. The "differential" exponent (1) declines to the value of zero at the turbidity maximum and inverts its sign beyond it. Within a limited size range - defined by m - a closely related, but faster method suggests itself, i.e. the mere scanning of the turbidity spectrum in order to locate the wave length of maximum turbidity. The scope and limits of practicality of the procedure follow from Table 3 which gives the theoretical diameter of the particles, D_M^0 , associated with a maximum turbidity at the respective wave length, λ_c , if $m = 1.20$.

Table 3

λ_c (A.U.):	7000	6500	6000	5500	5000	4500	4000	3500
D_M^0	1.30	1.20	1.11	1.02	0.926	0.833	0.741	0.648

Whichever of the three related methods is chosen to avoid bivalued results, it is desirable to know beforehand the location of the maximum for a given m . From the data given in Table 1, and previously (1), an empirical equation can be derived which allows to pinpoint the maximum at any m , viz.

$$(1) \alpha_M = \alpha_\infty + \alpha_c e^{-bm}$$

α_M represents the α -value at the turbidity maximum, if $\lambda_0 = 5461$ A.U. The equation is tested in Table 1 where the second and fourth columns give, respectively, the α -value at the turbidity maximum as found or interpolated from the theoretical curves (cL_M^0) and the particle diameter, D_M , corresponding to α_M . The values with asterisks apply to aerosols rather than liquid dispersions and were calculated from alternate light scattering functions (6). Their inclusion demonstrates the wide range of usefulness of equation (1).

Table 4

m	α_M^o	α_M	D_M
1.05	—	16.65	2.172
1.10	—	11.15	1.455
1.15	10.0 ± 0.5	10.01	1.306
1.20	7.8 ± 0.2	7.75	1.011
1.25	6.05 ± 0.05	6.12	.798
1.30	5.00	5.00	.652
1.35	—	4.20	.548
1.40	$4.0 \pm 0.5^*$	3.63	.474
1.45	—	3.23	.421
1.50	$3.25 \pm 0.25^*$	2.94	.384
1.55	—	2.74	.357
1.60	$2.5 \pm 0.25^*$	2.60	.339

The first turbidity maximum is followed by a first minimum, beyond which D- values derived from $(\bar{\tau}/c)_o$ are triplevalued. This cannot be expected, however, for α - values smaller than 20 ± 2 , ($D \sim 2.5$ microns) if $m = 1.20$ ($\lambda_o = 5461$ A.U.). This further complication is immaterial because particle size measurements from turbidity lose rapidly interest above $\alpha = 15-20$ on account of a fast increasing insensitivity of $(\bar{\tau}/c)_o$ to particle size.

The strong variation of D_M with m , at a given λ_o , implies a strong variation of λ_{opt} - the wave length at which the turbidity maximum occurs - with m , at a given D . Considering for example $D = 1.000$ microns, the turbidity maximum, in water at 25°C , should occur at $\lambda_o = 4182, 5401$

and 6840 A.U. if $m = 1.15$, 1.20 and 1.25 respectively. Locating the first turbidity maximum by means of turbidity spectra should therefore afford a simple and quite precise method for determining the refractive index, μ of the light scattering material if the diameter is known from an independent method, e.g. electron microscopy. The $I_{\text{out}}(m)$ curve indicates that locating the maximum with an uncertainty of ± 30 A.U. should give μ with an uncertainty not to exceed ± 0.001 .

Finally, it is noteworthy that non-monochromatized light of an incandescent source, observed through a liquid dispersion of scattering dielectric spheres, should possess nearly complementary colors above and below the turbidity maximum affording a rapid visual check of the minimum or maximum particle size present in a fairly monodisperse system. Considering again $m = 1.20$, the transmitted light should have a purple, greenish or bluish tinge for $D > 1.0$ and < 2.3 microns while it is red, orange or yellow--depending on concentration and layer thickness--if $D < 1.0$ microns. An important practical implication is that the emission of yellow radiation instead of white light, cf equal total intensity, may under proper circumstances critically reduce signals of an object approaching through a turbid environment contrary to the opposite view generally held. No problem exists for D - values in excess of 2.5 microns since the attenuation of visible radiation by a turbid medium is then largely independent of wave length.

* This work was carried out with the support of the Office of Naval Research.

- (1) W.Heller and W.J.Pangonis; J.Chem.Physics 22, 943 (1954).
- (2) Computation of the primary functions, from which the data given here are derived, were carried out by the Computation Laboratory of Wayne University (using the Unitized Digital Electronic Computer, UDEC). These functions, together with previous ones (1) computed manually by W.J.Pangonis will appear shortly elsewhere.
- (3) The meaning of symbols and the conditions under which numerical values given apply, were previously defined (1), except for c which in both instances represents the concentration of light scattering material, in g per 100 g of dispersed system. It may be added that experimental $(\bar{Z}/c)_o$ - values, to agree with the theoretical ones, must be extrapolated to infinite dilution and apply to a layer of 1.0 cm.
- (4) This term is proposed to supersede the term "Tyndall spectrum", previously introduced (5), in those instances where the wave length dependence of transmitted light rather than that of the laterally scattered light is meant. In spite of the intimate relation between the two wave length functions, their differentiation in terminology is advisable in order to avoid misunderstandings.
- (5) W.Heller and E.Vassy; J.Chem.Physics 14, 565 (1946).
- (6) Light scattering functions for spherical Particles; R.O.Gumprecht and C.M.Sliepcevich; University of Michigan (1951).